SYNOPSIS

Ph.D in Physics

Photodegradation, Anti-bacterial and Self-cleaning Analysis of Surface Modified Zinc Oxide and its Composites for Environmental Remediation

Submitted by

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1. INTRODUCTION

Water contamination directly impacts human health, wildlife and marine ecosystems. A wide variety of pollutants severely compromises water quality [1]. Organic contaminants such as pharmaceuticals, phenol, and carcinogenic dyes while, inorganic contaminants like heavy metals collectively degrade water resources. The discharge of untreated industrial effluents into water bodies is the primary cause for water pollution. This depletes the levels of dissolved oxygen creating inhabitable condition for aquatic life and posing risks to human health. Numerous techniques such as filtration, osmosis, chlorination, chemical oxidation, and biofiltration are used to address water pollution. But, these methods pose few drawbacks such as time consumption, expensive, complex operations, and harmful by-products limit their effectiveness [2]. Therefore, there is increasing demand for efficient eco-friendly alternative methods like biological treatment, green oxidants and advanced oxidation processes for environmental remediation.

Nanotechnology has revolutionized photocatalysis by enabling creation of materials with significantly enhanced properties. Reducing material dimensions to nanoscale level amplifies light absorption ability and catalytic activity [3]. Removal of organic pollutants for water systems can be done by developing nanomaterials as adsorbents. Nanoparticles possess larger surface area increasing the number of surface active sites producing more hydroxyl radicals, which enhances the efficiency of photocatalysis. Semiconductor photocatalyst offers promising means for sustainable solutions, which are cost-effective environmental remediation, and carbon dioxide reduction.

Surface modification of the photocatalyst enhances its stability, and photocatalytic activity. Other metal precursors as well as polymers acts as surface modifiers. It aims in reducing surface energy and prevents aggregation, while enhancing properties of photocatalyst [4, 5]. Their surface chemistries along with functionalization with specific groups allows removal and detoxification of pollutants. Changes in the morphological and optical properties aids in pollutant degradation [6]. Metal and metal oxide based nanomaterials excels in removing organic pollutants that harm the environment. Increased adsorption capacity and rapid kinetics contribute to high photodegradation efficiency.

Silane modifiers creates robust chemical bonds between organic and inorganic materials. These silane modifiers ($X(CH_2)_nSiR_3$) possess two separate functional groups, Organic functional

group reacts with organic materials, while the hydrolysable groups (R) interacts with elements like methoxy, ethoxy, etc., which are intermediates and forms silanol groups to create bonds with inorganic material or nanoparticle surfaces. Silica based nanomaterials have shown promising solutions for environmental remediation. They possess high surface area, enhanced pore volume, adjustable pore size and easily surface modifiable [7]. Reduction in recombination rate can be attained by surface modification of the photocatalyst and also reduces agglomeration of metal oxide.

Nanocomposites with ideal bandgap energy, structure, and reactivity exhibit enhanced photocatalytic activity. Likewise, metal oxide thin films with different morphologies exhibit significant potential for both environmental remediation and optoelectronic applications. Band gap energy of ZnO (3.37 eV) is ideal for self-cleaning applications under solar irradiation. Zinc oxide effectively breaks down organic contaminants and promotes water dispersion across the surface of the catalytic film, enabling its self-cleaning functionality upon light illumination [8]. Flat, uniform, optically transparent, photocatalytically active, highly crystalline nature of ZnO thin films helps to overcome the reduced visibility usually encountered in self-cleaning surface coatings. The work aims at preparation of environmentally stable and reusable photocatalytic material for reducing environmental degradation.

- Synthesis of suitable nanomaterial for photodegradation analysis by sol-gel technique.
- Evaluation of photocatalytic performance of nanocomposites for MB, MG and textile dye effluent degradation.
- To evaluate anti-bacterial efficacy of the nanocomposites.
- Fabrication of roughness enhanced transparent hydrophobic thin films for self-cleaning application.
- Fabrication of metal doped thin films for evaluation of Stearic acid degradation.

2. FRAME WORK OF THE THESIS

- **Chapter I** highlights the increasing demand for efficient eco-friendly alternatives and the evolution of nanotechnology in aiding advanced oxidation process by semiconducting materials for environmental remediation.

- **Chapter II** provides a detailed account of the processes available in material identification, synthesis and characterization techniques with a focus on promoting photodegradation, antibacterial and self-cleaning ability.
- **Chapter III** provides comprehensive overview of the materials and methods used in nanoparticle synthesis and thin film fabrication.
- **Chapter IV** presents a detailed analysis of the synthesized nanomaterials: Pristine ZnO, ZnO/PEG, ZnO/PEG/MTMS, ZnO/PEG/MTES, ZnO/PEG/VTMS and ZnO/PEG/VTES.
- **Chapter V** investigates photodegradation of Methylene Blue, Malachite green and textile dye effluent by the synthesized nanocomposites upon visible and UV light irradiation.
- **Chapter VI** reports anti-bacterial efficacy of pristine and surface modified composites of ZnO.
- **Chapter VII** investigates wetting behaviour and self-cleaning ability of transparent surface coatings based on silane/polymer composites.
- **Chapter VIII** examines photodegradation of Stearic acid using metal oxide-based silane/polymer thin films under UV irradiation.
- **Chapter IX** summarizes findings of the conduced research.

3. MATERIALS AND METHODS

Polymeric surfactant PEG-4000 and various silanes were used for functionalization of Zinc Oxide. The chemicals used for preparation, surface modification of metal oxide nanoparticles and fabrication of thin film are Zinc acetate dihydrate, Polyethylene glycol – 4000 (PEG 4000), Methyltrimethoxysilane (MTMS), Methyltriethoxysilane (MTES), Vinyltrimethoxysilane (VTMS) and Vinyltriethoxysilane (VTES). Homogenous materials with high purity were produced using sol-gel method. The dyes used were Methylene Blue (MB), Malachite green (MG) and textile dye effluent from textile industry operating in Tirupur, Tamil Nadu.

Synthesis of ZnO nanomaterials:

The precursors, zinc acetate dihydrate and sodium hydroxide in a ratio of 1:4 was added to 10ml and 15ml of deionized water respectively and stirred separately at 40^{o}C using a magnetic stirrer for 30 mins. The homogenous sodium hydroxide solution was added dropwise into zinc acetate dihydrate sol, the solution turned milky white and was subjected to stirring for continuous 2 h. Upon aging for an hour at room temperature, the obtained precipitate was washed several

times using deionized water and filtered using Whatmann filter paper. The residue was subjected to drying at 80°C in a hot air oven and calcinated at 200°C in muffle furnace for 2 h. The synthesized sample was ground into finer particles using a mortar and pestle, and labeled as ZnO.

Surface modification of ZnO nanomaterials by polymer and polymer/silane:

The synthesized Zinc oxide nanoparticles were functionalized using Polyethylene glycol 4000 (PEG 4000). An optimized amount of ZnO was dispersed in ethanol (0.085 M) by continuous stirring at 60°C using a magnetic stirrer for 30 mins. To the dispersed sol, PEG 4000 (2.5×10^{-4}M) was added and stirred for 90 mins. The obtained suspension was aged for an hour. The precipitate was washed with ethanol and filtered. For hybridization of the sol by silane, silica precursors MTMS (3.5×10^{-3}M), MTES (2.5×10^{-3}M), VTMS (3.3×10^{-3}M) and VTES (2.4×10^{-3} M) was added drop by drop using a dropper individually to separate sols of ZnO/PEG and further stirred for an hour to attain complete dissolution of the precursors. Upon aging for an hour, white precipitate from the suspension was washed several times using ethanol and filtered. The filtrate of ZnO/PEG and ZnO/PEG/Silane were each dried separately at 80°C in hot air oven for an hour and further annealed at 200°C using muffle furnace for a duration of 2 h. The obtained samples were ground with a mortar and a pestle and labeled accordingly.

Fabrication of silane/polymer and silane/polymer/metal oxide doped thin films:

Silane/PEG 4000 and ZnO/PEG 4000/Silane thin films were fabricated by sol-gel method using spin deposition technique. Initially, ethanol, hydrochloric acid and deionized water in the molar ratio $0.08:1.65\text{x}10^{-3}:0.05$ were stirred with a magnetic stirrer at room temperature. Then an optimized amount of the polymer (PEG 4000) was added to the acid sol and stirred for 30 mins. After which, silica precursors of optimized quantity were added and stirred further for 2 h to attain a homogenous sol. The obtained transparent Silane/Polymer sol was kept for aging at room temperature for 2 hrs. On aging, the sol was used for deposition.

For the synthesis of Metal Oxide/Polymer/Silane sol, Ethanol (0.08 M), Hydrochloric acid ($1.65\text{x}10^{-3}$ M) and Deionized water (0.05 M) was stirred for a few minutes. To the acidic medium, Zinc acetate dihydrate ($4.5\ \text{x}10^{-4}$ M) was added and stirred for 30 mins. For functionalization of ZnO, polymer (PEG 4000) was added and stirred continuously for 30 mins. Later, optimized amount of silica precursors was added dropwise and stirred for 2 h. The hybridized homogenous

sol was left undisturbed at room temperature for 2 h for gelation. After which, the hybridized sol was deposited onto cleaned glass substrates by spin coating technique. Both the silane/polymer and metal oxide/polymer/silane coated transparent films were annealed at 150^{o}C for an hour using muffle furnace for solvent evaporation and to increase the adhesion of the coatings to the substrate.

Preparation of Stearic acid modified coating:

Stearic acid modification on Silane/Polymer/Metal oxide thin film was done by spin coating technique. The Stearic acid sol was prepared using Ethanol (0.08 M) and Stearic acid ($3.51x10^{-4}$ M) was stirred for 1 hr and aged at room temperature for 1 hr. After which, the sol was deposited onto metal oxide/polymer/silane coated glass substrates by spin coating technique. The film was annealed at 120^{o}C for an hour using muffle furnace.

Experimental procedure for photodegradation analysis by metal oxide nanocomposites:

For dye degradation analysis by batch technique, 1.56×10^{-4} M of MB dye and 0.5×10^{-3} M of MG dye were added separately to 100ml water and stirred in dark environment for a duration of 30 mins. The synthesized nanomaterials were added to the dye solution and dispersed using a magnetic stirrer for 30 mins to attain adsorption-desorption equilibrium. Halogen lamp 50W (Philips) as visible light source of wavelength ~360nm with luminous efficacy of 85.9 lm/W and 10W UV light source (Philips) of wavelength ~254nm with luminous efficacy of 80 lm/W was used. The sample was subjected to illumination from a distance of 10cm. At an interval of 5 mins, 5ml of the test sample was drawn, centrifuged (2500 rpm, 3 mins) and the resultant supernatant liquid was further analyzed using UV-Visible Spectrophotometer.

4. MATERIAL ANALYSIS TECHNIQUES

The presence of various functional groups in the synthesized samples were confirmed using Fourier Transform Infrared (FTIR) spectroscopy over the range 400-4000cm^{-1} (SHIMADZU). Using X-ray diffraction analysis, the structure and the crystallite size of the samples were analyzed with a 2Θ range 10^{o}-80^{o} (Bruker D8 Advance diffraction with CuKα radiation). Field Emission Scanning Electron Microscopy (FESEM) to study the surface morphology and Energy Dispersive Spectroscopy (EDS) to estimate the elemental composition (SIGMA HV-Carl Zeiss with Bruker Quantax 200, Z10 EDS Detector). The energy band gap analysis of the synthesized nanomaterials was assessed using UV-vis Diffuse Reflectance Spectroscopy (DRS) (V-770 UV-Visible NIR

spectrophotometer, Jasco). The optical emissions were assessed using Spectrophotofluorometer (RF 5301 PC). Degradation efficiency of the nanocomposites for organic dyes and textile dye effluent was evaluated with UV-Visible Spectrophotometer (V-670 spectrophotometer, Jasco). Antibacterial activity of the samples was analyzed using agar well diffusion method for various pathogens such as Staphylococcus aureus (S.aureus) and Bacillus cereus (B.cereus), and gram negative bacterial species such as Escherichia coli (E.coli) and Pseudomonas aeruginosa (P.aeruginosa). Using 3D Laser Zeta Profilometry, roughness analysis of the coated surfaces was done. Wetting behaviour of the surface was assessed using contact angle measuring unit (OCA20) using water. Removal of Stearic acid by photo-induced catalysis of metal oxide doped polymer/silane thin films was evaluated by observing the changes in peak intensity and wettability using FTIR and water contact angle analysis, respectively.

5. RESULTS AND DISCUSSION

5.1 Fourier Transform Infrared Spectroscopy Analysis

Confirmation about the presence of functional group, bonding types and molecular presence has been done by FTIR analysis. Infrared radiation is passed through the sample and absorption of the radiation of specific wavelength occurs, which changes the dipole. The vibrational freedom of the molecule is determined by the absorption peaks obtained. The presence of OH radicals that are the primary oxidizing agents for dye removal was confirmed in all the synthesized composites.

5.2 X-Ray Diffraction Analysis (XRD)

X-Ray diffraction analysis provides information about the atomic and molecular structure, orientation of the crystal and crystallite size. Atoms are three dimensional structures, arranged in the form of an array, with no change in orientation or rotation. Such regular arrangement of atoms within a crystal represents a lattice. The crystallite structure of the synthesized ZnO nanomaterial and its corresponding physical states were identified based on the position, intensity and sharpness of the obtained diffraction peaks. The diffraction patterns at 2θ values 31.7º, 34.4º, 36.2º, 47.5º, 56.5º, 62.8º, 66.3º, 67.8º, 69.1º correspond to the hkl planes (100), (002), (101), (102), (110), (103), (200), (112), (201) respectively exhibiting crystallinity and were indexed as Hexagonal wurtzite structure of ZnO. The diffraction peaks that have been detected are in full agreement with the

standard values (JCPDS card no. 89-1397). Crystallite size was calculated using the Debye-Scherrer formula

$$D_{hkl} = \frac{k \times \lambda}{\beta_{hkl} \times \cos\theta_{hkl}}$$

Where, D_{hkl} represents the particle size perpendicular to the normal line of the hkl plane, β_{hkl} is the FWHM of the diffraction peak, θ_{hkl} is the Bragg's angle of the peak, k signifies the shape factor (0.89) and, λ represents wavelength of the CuKα x-ray source. The FWHM value of surface modified ZnO was increased than Pristine ZnO indicating significant reduction in size [9]. Crystallite size of Pristine ZnO, ZnO/PEG, ZnO/PEG/MTMS, ZnO/PEG/MTES, ZnO/PEG/VTMS and ZnO/PEG/VTES were 42nm, 38nm, 28nm, 27nm, 17nm and 21nm, respectively. The average crystallite size of polymer and polymer/silane doped ZnO is lesser than Pristine ZnO, which might lead to reduction in the particle size. For metal oxide doped silane/polymer thin films, the average crystallite was 36nm for ZnO/PEG/MTMS, 38nm for ZnO/PEG/MTES, 37nm for ZnO/PEG/VTMS and 34nm for ZnO/PEG/VTES.

5.3 Field Emission Scanning Electron Microscopy (FESEM) and EDX Analysis

FESEM is an advanced surface analytical technique that provides topographical information. It captures the microstructural image of the material. FESEM image revealed anisotropic hexagonal morphology of the synthesized pristine ZnO nanomaterial with particle size of 216 nm. Agglomerated semi-cubic morphology of ZnO/PEG with average particle size as 147 nm which was lesser than pristine ZnO was noted. The addition of polymer to the surface of the metal oxide reduced its particle size. The uncharged hydrophilic residues and significant surface mobility of PEG results in steric exclusion, therefore PEG on the surface of the metal oxide enhances photostability. Average particle size of ZnO/PEG/MTMS, ZnO/PEG/MTES, ZnO/PEG/VTMS and ZnO/PEG/VTES were 112nm, 117nm, 102nm and 109nm, respectively. The addition of polymer and silane modifies the surface, reduces particle size and aggregate formation of the metal oxide. Silane coupling agents acts as surface modifiers to ZnO nanoparticles. Certain organosilicon compounds exhibit two different functional groups, one of which reacts with inorganic substances and the other with organic substances [10].

Surface morphological analysis of Silane/Polymer thin films revealed that the surface had crack-free morphology and uniform. FESEM imaging of ZnO/PEG/MTMS film revealed smooth morphology with homogenous pores, whereas for ZnO/PEG/MTES, ZnO/PEG/VTMS and ZnO/PEG/VTES films demonstrated porous morphology with particle distribution throughout the surface.

Energy dispersive X-ray spectroscopy, a technique to determine the elemental composition of the material. Spectral intensity ascertained the number of elemental presence in the material under analysis. The analysis revealed that synthesized nanomaterial contained their corresponding elements and were found to be free from impurity.

5.4 UV-DRS

The bandgap energy of the synthesized nanomaterials was analyzed between the wavelength range 300-800nm by UV-Vis Diffuse Reflectance Spectroscopy. Using Kubelka-Munk function, optical bandgap energy of ZnO nanomaterial was calculated with the axis of photon energy.

$$[F(R)h\upsilon]^2=C(h\upsilon - E_g)$$

Where F(R), known as the Kubelka-Munk function, is the ratio of molar coefficient of absorption to the scattering factor, which represents the absolute reflectance. For the estimation of band gap energy, Tauc plot was extrapolated with a straight line between the axis $[F(R)h\upsilon]^2$ and $E_g=\frac{hc}{\lambda}$. Optical bandgap energy of the synthesized ZnO, ZnO/PEG, ZnO/PEG/MTMS, ZnO/PEG/MTES, ZnO/PEG/VTMS and ZnO/PEG/VTES nanomaterials were 3.192 eV, 3.181 eV, 3.173 eV, 3.167 eV, 3.134 eV and 3.151 eV, respectively.

5.5 Photoluminescence Spectroscopy

Photoluminescence spectra of a semiconductor material is due to the recombination of photo-induced charge carriers. Several defects in the surface and oxygen vacancies can be identified from PL spectrum. Higher PL intensity signifies greater recombination of photo-induced electron-hole pairs [11]. Luminescence of the composites was assessed at room temperature ($30^{\circ}C$) for the excitation wavelength (λ_{exc}) 330nm. Emissions were observed at 452nm, 470nm, 484nm and 490nm. The band at 452nm corresponds to blue emission due to the occurrence of neutral

oxygen vacancies [12]. The peak at 470nm is attributed to the blue emission due to the intrinsic defects emission in Zinc interstitial (Zn_i) [13]. The blue emission band at 484nm is typically explained by the radiative recombination of an electron that occupies the oxygen vacancy with a photogenerated hole [14]. The peak at 490nm is attributed to blue-green emission due to the recombination of electron-hole pairs within the material [15].

5.6 UV-Visible Spectroscopy

Using nanomaterials, degradation analysis of Methylene Blue, Malachite Green and textile dye effluent (Reactive Red) under Visible and UV light illuminations was performed and the samples were tested for dye removal using UV absorbance spectra. The dye degradation efficiency of Pristine ZnO for MB was 36.5% (Vis) and 37% (UV), for MG 55% (Vis) and 48% (UV). Degradation efficiency of ZnO/PEG for MB was 52% (Vis) and 41% (UV), for MG 66% (Vis) and 54% (UV). Degradation efficiency of ZnO/PEG/MTMS for MB was 80% (Vis) and 76% (UV), for MG 78% (Vis) and 71% (UV). Degradation efficiency of ZnO/PEG/MTES for MB was 83% (Vis) and 79% (UV), for MG 82% (Vis) and 78% (UV). Degradation efficiency of ZnO/PEG/VTMS for MB was 92% (Vis) and 84% (UV), for MG 89% (Vis) and 83% (UV). Degradation efficiency of ZnO/PEG/VTES for MB was 83% (Vis) and 78% (UV), for MG 82% (Vis) and 78% (UV). Among all the combinations, maximum degradation efficiency was observed for the composite ZnO/PEG/VTMS due to its reduced PL intensity signifying reduced recombination rates. ZnO/PEG/VTMS for textile dye wastewater (Reactive red) degraded 73% under visible and 65% under UV light illumination. The composite was also found to be photo-stable exhibiting 69.9% and 62% (Cycle-5) under visible and UV light. Therefore, ZnO/PEG/VTMS demonstrated high photostability and is reusable for multiple cycles, which works as an excellent photocatalyst for dying industry effluent water.

5.7 Anti-bacterial Analysis

Antibacterial activity of the synthesized nanomaterials was analyzed against the gram positive and gram negative bacterial strains Staphylococcus aureus, Escherichia coli, Bacillus cereus and Pseudomonas aeruginosa using agar well diffusion method. Teicoplanin **(**TEI^{30} susceptibility test disc 30mcg**)** was used as positive control. Antibacterial test was outsourced from "Advanced Research Laboratory" of our Institute. Polymer and silane/polymer doped metal oxide nanocomposites exhibited better antibacterial activity than Pristine ZnO because surface

modification of ZnO considerably reduced the particle size, resulting in more specific surface area of the composite [16].

5.8 3D Laser Profilometry and Wettability Analysis

Surface roughness is a microscopic measure of the deviations and inherent irregularities on the surface. The films were assessed using 3D optical profilometer to measure the height of the surface at regular intervals. Roughness plays a major role in the wettability of the surface. Wettability of the surface can be evaluated by measuring the angle formed in the region of contact between the water and solid interface [17, 18]. Surface roughness and water contact angle analysis revealed an average roughness of 0.3920µm with 105.3º for MTMS/PEG, 0.5049µm with 107º for MTES/PEG, 0.3333µm with 94.9º for VTMS/PEG and 0.3598µm with 97.5º for VTES/PEG composite films. Average roughness and water contact angle analysis of ZnO/PEG/MTMS was 0.7644µm with 108.3º, ZnO/PEG/MTES was 0.4150µm with 106.5º, ZnO/PEG/VTMS was 0.2772µm with 90.3º and ZnO/PEG/VTES was 0.3537µm with 95.7º.

6. CONCLUSION

- Nanocomposites of ZnO and transparent hydrophobic silane/polymer and metal oxide/polymer/silane thin films were produced using sol-gel technique and characterized by FTIR, XRD, FESEM, EDS, UV-DRS, PL, UV-Visible, Surface roughness and Water contact angle analysis.
- All Silane/Polymer doped ZnO nanocomposites exhibited enhanced photo degradation activity than its Pristine and Polymer doped counterparts. ZnO/PEG/VTMS demonstrated high photostability and reusability.
- Antibacterial efficacy of all synthesized nanomaterials were analyzed by agar well diffusion method. All composites of ZnO demonstrated better antibacterial efficacy against selected bacterial pathogens when compared to the control used.
- Transparent hydrophobic silane/polymer thin films exhibited self-cleaning behaviour against sand particles, upon interaction with water droplets.
- Stearic acid was deposited on Metal Oxide/Silane/Polymer film, which degraded upon UV irradiation was then confirmed by FTIR and water contact angle analysis.

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